X-ray Diffraction Study of Some Normal Alkyl Esters of Long-Chain Acids[1]

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2617

ABSTRACT

X-ray powder diffraction data are reported for 15 normal long-chain esters. The compounds represent all combinations of acid and alcohol where the acid portion is n-tetradecanoic, n-hexadecanoic, or n-octadecanoic acid, and the alcohol portion is n-tetradecanol, n-pentadecanol, n-hexadecanol, n-heptadecanol, or n-octadecanol. The individual compounds can be identified and distinguished by the diffraction data. Several of the esters have long spacings that are a linear function of the number of carbon atoms in the molecule and are consistent with a similar function for ethyl esters of long-chain acids. The remainder of the compounds crystallize in other polymorphic forms and therefore do not follow this function.

INTRODUCTION

KOHLHAAS (4) HAS REPORTED the unit cell and space group for hexadecyl hexadecanoate. The methyl and ethyl esters of normal long-chain acids were characterized by powder diffraction by Malkin (6), Francis et al. (2, 3) and Piper et al. (10). However little is known about the crystallography of higher homologs of normal aliphatic esters. This paper reports x-ray diffraction studies for 15 normal long-chain aliphatic esters whose general formula is $CH_3(CH_2)_nCOO(CH_2)_mCH_3$ where n is 12, 14, or 16, and m is 13, 14, 15, 16, or 17. All compounds under study are solid crystalline materials, the melting points of which are above room temperature and therefore suitable for study by x-ray diffraction.

EXPERIMENTAL

Materials and Methods

Sample Preparation. Observed melting-points and literature values (11) for these compounds are included in Table I. The majority of the samples were purchased from Lachat Chemicals Inc. Two samples (octadecyl tetradecanoate and octadecyl octadecanoate) were synthesized at this Laboratory. The commercial samples had to be washed to remove unreacted acids. The odd-chain alcohol esters had to be further purified by passing through a column of silicic acid to remove both unreacted alcohol and acid. Thin-layer chromatography showed no trace of alcohol and acid after this treatment. The samples were then crystallized three

[1] Presented at AOCS Meeting, Philadelphia, October 1966.
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TABLE I
Long Spacings of Normal Alkyl Esters of Long-Chain Acids

Name of compound	Melting point (observed)	Melting point (literature)	Total carbon atoms in molecule	Long spacing Å	No. of orders used
Tetradecyl tetradecanoate	39.1—39.8		28	34.54 ± 0.06	14
Pentadecyl tetradecanoate	45.8—46.4		29	36.70 ± 0.15	4
				35.76 ± 0.05	4
				35.16 ± 0.08[a]	5
				32.67 ± 0.12[b]	3
Tetradecyl hexadecanoate	49.5—49.8		30	36.79 ± 0.01	13
Hexadecyl tetradecanoate	46.4—46.5		30	41.36 ± 0.04	8
Pentadecyl hexadecanoate	55.8—56.4	55.5	31	37.62 ± 0.01	13
Heptadecyl tetradecanoate	50.6—51.4		31	39.83 ± 0.05	8
				37.83 ± 0.06[b]	5
Tetradecyl octadecanoate	51.2—51.8		32	43.44 ± 0.01	14
Hexadecyl hexadecanoate	49.8—50.4	51.6	32	38.90 ± 0.01	15
Octadecyl tetradecanoate	50.5		32	38.98 ± 0.02	16
Pentadecyl octadecanoate	55.4—55.8		33	39.75 ± 0.01	20
Heptadecyl hexadecanoate	57.6—58.2		33	39.84 ± 0.02	18
				36.74 ± 0.08	5
Hexadecyl octadecanoate	57.0—57.6		34	41.34 ± 0.02	15
Octadecyl hexadecanoate	58.3—58.8	59.0	34	45.98 ± 0.01	15
Heptadecyl octadecanoate	65.0—65.6	64.7	35	42.08 ± 0.01	20
Octadecyl octadecanoate	62	62	36	43.47 ± 0.02	18

[a] Found only in spectra taken from melt.
[b] Found only in spectra taken from acetone.

TABLE II
Relative Intensity of Orders of 001 (Long Spacing)

Name of compound	Relative intensities of orders of long spacing						
	1	2	3	4	5	6	7
Hexadecyl hexadecanoate	1000	35	550	15	196	10	63
Octadecyl tetradecanoate	1000	178	375	275	13	174	2
Heptadecyl tetradecanoate	1000	71	158	79	10	36	<4
Pentadecyl octadecanoate	1000	4	460	2	195	3	91
Heptadecyl hexadecanoate	1000	22	373	63	85	106	16
Hexadecyl tetradecanoate	1000	55	365	70	65	53	6
Hexadecyl octadecanoate	1000	36	496	16	196	11	55
Tetradecyl octadecanoate	1000	22	500	40	190	50	58
Octadecyl octadecanoate	1000	7	284	6	96	4	30

times from an acetone solution before x-ray diffraction patterns were taken.

Each compound was crystallized from the melt and also from acetone at room temperature. In most cases the same form was obtained by both procedures. X-ray diffraction measurements were made with a General Electric XRD-3 direct-recording unit, using nickel-filtered CUKα radiation ($\lambda = 1.5405$ Å), 1° beam slit, 0.1° detector slit, medium resolution sollar slit, scanning speed 0.2° per minute, chart speed 12 in. per hour, linear scale, 8-seconds time constant. The x-ray data listed in Table I were obtained from unground samples. Thin layers, measuring approximately 0.5×1.0 in., were firmly pressed on a glass slide to insure adherence. The long spacings listed in Table I are the averages for the number of orders listed in column 6; column 5 also gives the 95% confidence limits. The first and sometimes the second orders were often not included because of the limited accuracy with which they could be measured. Complete x-ray powder patterns are not, in general, included because of the space required.

RESULTS AND DISCUSSION

All the compounds investigated can be identified and distinguished by the x-ray diffraction powder data. Normally the long spacing alone is sufficient for identification. However examination of Table I reveals a few sets of compounds with almost identical long spacings: hexadecyl hexadecanoate and octadecyl tetradecanoate; pentadecyl octadecanoate, heptadecyl hexadecanoate (form with larger long spacing), and heptadecyl tetradecanoate (form with larger long spacing); hexadecyl tetradecanoate and hexadecyl octadecanoate; and tetradecyl octadecanoate and octadecyl octadecanoate. In these cases the compounds can be identified and distinguished by gross differences in the relative intensities of the long spacing orders (Table II). For example, examination of Table II shows that, for hexadecyl hexadecanoate, the fourth order is much weaker than the fifth order whereas for octadecyl tetradecanoate the reverse is true, thus permitting the two esters to be distinguished. Likewise the other sets of compounds can be distinguished by the relative intensities of their long spacing orders. For example, in the x-ray powder pattern of heptadecyl tetradecanoate, the fourth order is much stronger than the fifth order and the seventh order is missing; in pentadecyl octadecanoate the fourth order is much weaker than the fifth order and the seventh order is present and strong; and in heptadecyl hexadecanoate the fourth and fifth orders are about the same intensity and the seventh order is present, though not very intense. These three can also be distinguished by the formation of the second phase on crystallization. Pentadecyl octadecanoate does not form a second phase; heptadecyl hexadecanoate forms a second phase (long spacing 36.74 Å) from both melt and acetone; heptadecyl tetradecanoate forms a second phase (long spacing 37.83 Å) from acetone but not from melt. In the case of hexadecyl tetradecanoate and hexadecyl octadecanoate, the sixth order is stronger than the seventh order for the tetradecanoate whereas the reverse is true for the octadecanoate. In the case of tetradecyl octadecanoate and octadecyl octadecanoate, the sixth and seventh orders are about the same relative intensity for the tetradecyl derivative, but the sixth order is much weaker than the seventh order for the octadecyl derivative.

Several of the esters have long spacings which are a linear function of the number of carbon atoms in the molecule. Tetradecyl tetradecanoate, tetradecyl hexadecanoate, hexadecyl hexadecanoate, octadecyl tetradecanoate, hexadecyl octadecanoate, and octadecyl octadecanoate fall on a straight line when the long spacing (y) is plotted against the number of carbon atoms in each molecule (x) as shown in Fig. 1. The least-squares equation of this line is $y = (3.1440 \pm 0.9588) + (1.1205 \pm 0.0298)\ x$. This would indicate that these es-

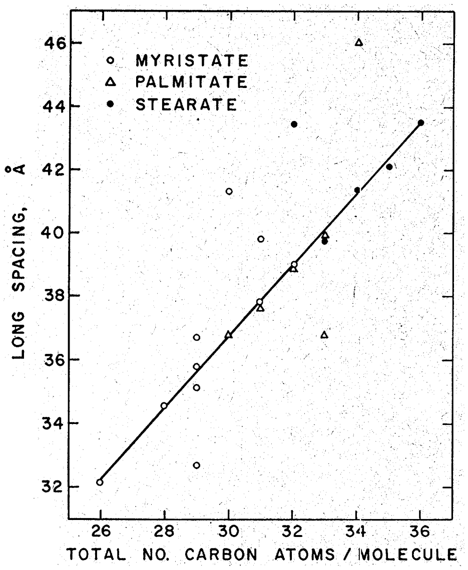

FIG. 1. Long spacing *versus* total number of carbon atoms per molecule for long-chain esters. Least-squares line derived from tetradecyl tetradecanoate, tetradecyl hexadecanoate, hexadecyl hexadecanoate, octadecyl tetradecanoate, hexadecyl octadecanoate, and octadecyl octadecanoate.

ters crystallize in the same polymorphic form. Therefore an attempt was made to index all reflections other than long spacings on the basis of the unit cell of hexadecyl hexadecanoate reported by Kohlhaas (4). It was assumed that all cell parameters remain constant except the c parameter, where the long spacing was taken as 0.5 c sin β. The attempt was successful, and the differences between observed and calculated values were within 0.01 Å. The characteristic side spacings seem to be the (110), (020), and (200) reflections in that order. It may be that the molecules lie on or near these planes.

A statistical analysis shows that the least-squares line of the above six compounds is indistinguishable from a least-squares line for the long spacing values of the ethyl esters of normal aliphatic acids (2, 3, 6). This would imply that the two series of compounds are isomorphous. Fortunately the unit cell of one of the ethyl esters is known, namely, ethyl stearate. The unit cell of ethyl stearate (8) seems to be isomorphous with that of hexadecyl hexadecanoate (4), but Kohlhaas reports the space group of hexadecyl hexadecanoate as $P2_1/a$ whereas Mathieson et al. report ethyl stearate as Ia. This would indicate that, although the unit cells are isomorphous, the structures are not.

If the long spacings of the six oxygen esters are compared with the values of the corresponding thiol esters (5), it is found that the long spacings of the corresponding sulfur compounds are greater on the average by 0.30 Å. This would be equivalent to an increase in the c parameter of about 0.68 Å. It may be assumed that the compounds are isomorphous and the same as hexadecyl hexadecanoate, that the covalent radii for oxygen and sulfur are those as given by Pauling (9), and that the aliphatic chain axis is roughly parallel to the c axis. If it is assumed that the asymmetric unit packs roughly as reported by Mathieson et al. (8), then the difference in the c axis between the corresponding sulfur and oxygen compounds should be about 1.18 Å. On the other hand, if it should be assumed that the asymmetric unit packs roughly, as suggested by Aleby for ethyl stearate (1), then the difference in c axis between corresponding sulfur and oxygen compounds would be about 0.50 Å. The observed 0.68 Å difference comes closer to the latter and would suggest that the compounds pack more nearly like the structure proposed by Aleby if the assumptions are correct. However, since the space group for ethyl stearate is different from the one reported for hexadecyl hexadecanoate, this conclusion is not certain without further study.

Normally an alternation in long spacing in a homologous series containing even and odd numbers of carbon atoms is typical of long-chain compounds (7). An examination of Fig. 1 seems to indicate that pentadecyl hexadecanoate, pentadecyl octadecanoate, heptadecyl hexadecanoate, and heptadecyl octadecanoate exist in the same polymorphic form. If their long spacing values are plotted against the total number of carbon atoms in each molecule (Fig. 1), it is seen that they do not fall in the same line with those containing an even number of carbon atoms but are slightly lower. Pentadecyl hexadecanoate, pentadecyl octadecanoate, and heptadecyl octadecanoate could be indexed by the same scheme as the evens, based on a unit cell of hexadecyl hexadecanoate. This would imply that the odd and even series are isomorphous. However the largest differences between observed and calculated values were greater than for the even series. The line representing the odd series would not necessarily be expected to coincide with that of the even series because of the difference in end packing between the two series. Further work is required in order to clarify this point.

If the long spacing values of these odd-chained compounds are compared with the values of the corresponding thiol esters (5), on the average the sulfur compounds have long spacing values greater by 0.36 Å with one value outstandingly high, 0.47Å. With the even series, the average difference between the oxygen and sulfur compounds was 0.30 Å; one value was outstandingly low, 0.20 Å. If both these extreme values were eliminated, the averages would be 0.33 Å for the odds and 0.34 Å for the evens. Perhaps each class of oxygen compounds bears the same relationship to the corresponding class of sulfur compounds. This cannot be definitely established without further study.

A graph of the long spacing values of the ethyl esters and long-chain acids (B form) (2,3,6) against the total number of carbon atoms per molecule (Fig. 2) shows that the values fall on two straight lines, one for the even and one for the odd series, with the line for the odd series above that of the even series. This is the reverse of findings for esters of long-chain alcohols and thiols. Perhaps a change in packing occurs between the ethyl derivatives and the higher homologs in the odd series.

An examination of Table I and Fig. 1 shows that the compounds with odd numbers of carbon atoms tend to display more polymorphic forms for each compound than in the even series, both in the total number of different forms and forms for each individual compound. The evens tend to crystallize in only one form, whether crystallized from acetone or melt, but the odds tend to display several forms under the same conditions. The odds seem to display at least five different polymorphic forms, probably a sixth if the forms of pentadecyl tetradecanoate and heptadecyl tetradecanoate with the largest long spacings are also different. This difference is suggested by the fact that a straight line drawn between these two points would have a negative intercept at zero number of carbon atoms.

Fig. 1 suggests that the polymorphic forms of pentadecyl tetradecanoate and heptadecyl hexadecanoate which exhibit the smallest long spacing values are the same crystalline forms, but it cannot be said with certainty without further study. Fig. 1 also suggests that hexadecyl tetradecanoate, tetradecyl octadecanoate, and octadecyl hexadecanoate crystallize in the same polymorphic forms, where the aliphatic chain axis would be almost parallel to the c

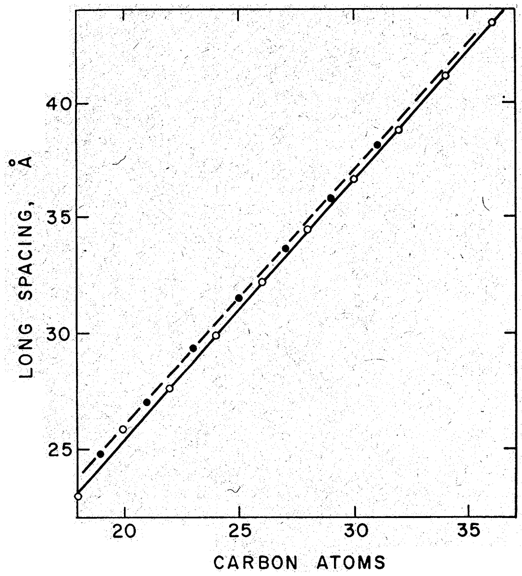

FIG. 2. Long spacing *versus* total number of carbon atoms per molecule, for ethyl esters of long-chain acids. Filled circles: Odd total number of carbon atoms. Open circles: Even total number of carbon atoms.

axis, but it cannot be established at this time without further study. Fig.1 shows that the form of heptadecyl tetradecanoate which displays the smaller long spacing value and one of the forms of pentadecyl tetradecanoate (second largest long spacing value) may crystallize in the same form as those isomorphous with hexadecyl hexadecanoate.

ACKNOWLEDGMENTS

Synthesis of the two compounds mentioned by S. G. Morris; chromatographic analysis by S. F. Herb and F. E. Luddy; consultation on statistical analysis by J. N. Boyd.

REFERENCES

1. Aleby, S., Acta Cryst. *15,* 1248 (1962).
2. Francis, F., S. H. Piper and T. Malkin, Proc. Roy. Soc. *128A,* 214 (1930).
3. Francis, F., and S. H. Piper, J. Am. Chem. Soc. *61,* 577 (1939).
4. Kohlhaas, R., Z. Krist *98,* 418 (1938).
5. Lutz, D. A., L. P. Witnauer, G. S. Sasin and R. Sasin, JAOCS *36,* 178 (1959).
6. Malkin, T., J. Chem. Soc. (London) 2796 (1931).
7. Malkin, T., Nature *127,* 126 (1931).
8. Mathieson, A. McL., and H. K. Welsh, Acta Cryst. *18,* 953 (1965).
9. Pauling, L., "The Nature of the Chemical Bond," 3d ed., Cornell University Press, Ithaca, N. Y., 1960, p. 224.
10. Piper, S. H., A. C. Chibnall and E. F. Williams, Biochem. J. *28,* 2175 (1934).
11. Ralston, A. W., "Fatty Acids and Their Derivatives," John Wiley and Sons Inc., New York, 1948, p. 757-758.